

Benzene Formation during Allene Pyrolysis:  
Possible Implications for Soot Formation

L. D. Pfefferle, J. Boyle, and G. Bermudez  
Department of Chemical Engineering, Yale University  
New Haven, CT 06520-2159YS

Introduction

Pyrolysis of allene in a microjet reactor at millisecond reaction times was used to study higher hydrocarbon growth processes from C<sub>3</sub> hydrocarbon species. Species detection was carried out using VUV photoionization mass spectrometry. The first product observed as temperature was increased at a fixed mean residence time was mass 80 followed by smaller than parent mass pyrolysis products, mass 79 and a possible allene trimer at mass 120. A mechanism for higher hydrocarbon formation in the pyrolysis of allene is proposed. Allene dimerization to a dimethylenecyclobutane is proposed as the initial higher hydrocarbon production mechanism during allene pyrolysis and this route is examined for thermodynamic plausibility.

Background

It has become increasingly apparent in the past several years that C<sub>3</sub> routes for soot formation in flames can be important under some if not many conditions. In several recent studies of fuel pyrolysis and combustion where both stable and labile product measurements were made (1a,b,2), C<sub>4</sub>/C<sub>2</sub> routes for benzene production were determined to be not fast enough to account for observed benzene production for some of the fuels used, especially those of C<sub>2</sub> and C<sub>3</sub> hydrocarbons. Westmoreland (1b) has recently made a reaction pathway study of C<sub>3</sub>H<sub>3</sub> dimerization to benzene using a QRRK analysis and concluded that this route could in fact be fast enough to account for observed benzene production rates in several test flames including acetylene and ethylene.

Allene dimerization to dimethylenecyclobutane isomers has been observed at high conversion in several early flow reactor pyrolysis studies (e. g. 3,4). In one study (3), primarily the 1,2-dimethylenecyclobutane isomer (1,2 DMCB) was produced at about 50% yield by passing allene over quartz chips at 800K with a 6s mean residence time. The reactor geometry used, however, did not preclude the possibility of significant surface effects on the rate of dimethylenecyclobutane production and a run with an empty tube reactor gave somewhat lower conversion but the same product distribution. In the current study, mass 80 was the first product detected and the detection of mass 120 (a possible allene trimer) at slightly higher temperatures is consistent with allene dimerization to dimethylenecyclobutane as the initial pathway for higher hydrocarbon formation. Although the DMCB isomers are likely the first mass 80 species formed, at higher temperatures (over 1300K) the predominant mass 80 component is likely hexadienes. The reaction pathways for formation of the various mass 80 isomers is the focus of our continuing modeling work. This study investigates the

feasibility of the DMCB production through allene dimerization and how it can contribute to early higher hydrocarbon production during allene pyrolysis. It should be noted that from our previous work (2) methyl acetylene pyrolysis when carried out at temperatures and reaction times where isomerization to allene was not significant did not result in either significant mass 80 production or benzene production. This is consistent with mass 80 formation through allene dimerization.

### Experimental Procedure

Allene pyrolysis was carried out in a microjet reactor source, described in detail earlier (5). This is a miniature fast-flow reactor coupled directly to a sonic nozzle with a volume of approximately  $3.2 \times 10^{-9} \text{ m}^3$ . The reactor geometry consists of an alumina multibore thermocouple insulator tube inserted into a larger alumina tube with a sapphire nozzle (50-200 mm). The inner tube is positioned to leave a reaction chamber 1 mm in length. Reactants (pure allene or allene/Ar in this study) are introduced to the pyrolysis zone through the center-most hole in the inner alumina tube (0.4 mm ID) at rates varying from 0.1 - 1.0 sccm. The reaction zone is resistively heated and temperature within the reactor zone has been calibrated using thermocouples. Thermocouples were not used continuously during experiments due to the catalytic oxidation/pyrolysis observed on the platinum/rhodium wires. Pressure within the microjet reactor was maintained at  $600 \pm 20$  torr. Under the stated operating conditions, wall reactions were not observed to significantly affect product distributions. Significantly lowering the pressure (by a factor of >10), however, leads to greater aromatic abundance at lower temperatures.

A schematic of the VUV photoionization mass spectrometer (VUV-MS) and microjet reactor assembly is illustrated in Figure 1. The TOF-MS is equipped with Wiley-McLaren type acceleration for higher resolution and an ion reflectron to compensate for initial ion energy spread, to provide a longer effective flight length (1 meter) and to prevent the considerable quantities of neutral polymeric hydrocarbons produced from reaching the detector. Mass signals are displayed in real time and recorded directly onto a digital storage oscilloscope which is interfaced with a PC for data analysis. The mass resolution for the experiments described herein was measured as 325 at 78 amu.

VUV photons were generated by the non-linear optical mixing technique of third harmonic generation in Xe. A frequency tripled Nd:YAG laser (Quanta Ray DCR-11 system) operating at 10 Hz was focused into a Xenon cell with a 30 cm path length at 26 torr. The signal from  $\text{C}_6\text{H}_6^+$  produced by single-photon ionization of  $\text{C}_6\text{H}_6$  from a 300 K fixed flow microjet expansion was used to monitor relative UV to VUV conversion efficiency. Optimum efficiency was found at approximately 30 mJ of energy in a 8 ns pulse at 354.6 nm, corresponding to a peak power of approximately  $3.75 \times 10^6 \text{ W}$ .

Ionization efficiencies at 118 nm are relatively constant (+/- 35%) and high for many five carbon hydrocarbons and larger, since these compounds have ionization potentials (IPs) of one to two eV below the photon energy ( $1182 \text{ \AA} =$

10.49 eV). Therefore the simultaneously-obtained peak ratios are good approximations of relative concentration. However for smaller hydrocarbons with ionization potentials lying closer to the single photon energy, absorption cross sections and ionization efficiencies vary considerably. Consequently, these species must be calibrated individually. Detection efficiencies of the various molecular hydrocarbons must likewise be considered to obtain quantitative data. These calibration issues have been presented in an earlier publication (5) and are discussed in detail in the PhD thesis of J. Boyle (6).

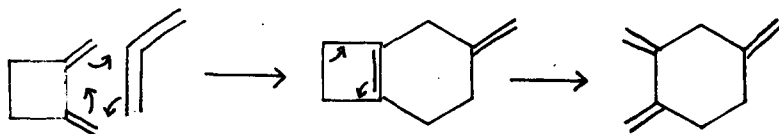
In our detection scheme only the molecular masses are detected, and the identity of structural isomers can only be inferred from arguments of internal consistency or knowledge of kinetic mechanisms and rate constants.

### Experimental Results and Discussion

An overview of the relative concentrations of higher than reactant mass hydrocarbons detected at 2ms mean reaction time is given in Table 1. As temperature was increased from 300K to 1200K at 2ms mean residence time, the first reaction product observed was mass 80 followed at slightly higher temperatures by reaction products smaller than the parent mass such as ethylene. Flow reactor results also indicate methane and hydrogen in significant quantities, although those products were not directly measured in this study due to their high ionization potentials (methane was indirectly measurable through its fragmentation product methyl radical). At 1320K mass 79 was detected above ppm levels and was observed to reach significant steady state concentrations prior to the appearance of mass 78. Benson and Shaw (7a,b) studied the pyrolysis of 1,3 and 1,4-hexadiene at low pressure and temperatures from 520 - 840K. These investigators found that while benzene production from 1,4-hexadiene proceeds through molecular elimination of hydrogen, the mechanism for benzene formation from 1,3-hexadiene proceeds via a chain mechanism involving hydrogen atoms, hexadienyl radicals and cyclohexenyl-3 radicals. The rate constant data reported is consistent with our mass 79 and benzene formation rates assuming our experimentally measured mass 80 concentration at 1450K contains a significant component of 1,3-hexadiene. This analysis suggests that a possible pathway for early benzene production during allene pyrolysis involves conversion of 1,2-dimethylenecyclobutane formed through allene dimerization to 1,3-cyclohexadiene as temperature is increased followed by a higher activation energy, slower conversion of cyclohexadiene to benzene through the cyclohexadienyl radical.

As temperature was increased above 1450K a broad range of hydrocarbons with 6 or more carbons were detected including mass 78, with the largest contributions initially coming from masses 91/92, 94, 106, 116-118, 120, 144 and 158. Mass 120 was possibly formed through reaction of a DMCB component of mass 80 with allene as noted in early work on the thermal polymerization of allene. Note that the mass 120 abundance decreases somewhat with temperature above 1515K. Mass 120 and 160, which are possible allene trimers and tetramers, were not seen in ethylacetylene pyrolysis but are present at significant levels in this study. At 1450K, mass 120 was observed in the next largest abundance to masses 80 and 79. This is another indication of allene dimer formation in this system. The mechanism

illustrated below was reported for allene dimer and trimer formation by Weinstein et al. who identified the structural isomers using NMR.



At higher temperatures and allene conversions, these species are converted through reactions with smaller hydrocarbons and hydrocarbon radicals such as  $\text{C}_2\text{H}$ . The early appearance of mass 144 suggests such a route.

#### Allene dimerization

Thermodynamic parameters for both 1,2 DMCB and 1,3 DMCB were estimated using the THERM program(9) and compared with experimental values where available. For 1,2 DMCB, the  $\text{DH}_{f298}^\circ = 47.3$  kcal/mol (calculated) and 48 kcal/mol (measured) and for 1,3 DMCB, the  $\text{DH}_{f298}^\circ = 51$  kcal/mol (calculated) and 53.3 kcal/mol (measured). These values are in good agreement (2-3kcal/mol lower) with the values calculated by Kovacevic and coworkers (10) using the maximum overlap method. These investigators also reported the experimental and calculated strain energy for 1,3 DMCB. From this data, equilibrium constants for the reactions  $2\text{Allene} \rightarrow 1,2 \text{ DMCB}$  and  $2\text{Allene} \rightarrow 1,3 \text{ DMCB}$  were calculated and are presented in Figure 2. The equilibrium constants for both reactions are greater than one at 1200 K. The rate of allene dimerization rate to 1,2-DMCB is pressure dependent and approximately 43.8 Kcal/mol exothermic.

#### Conclusion

A microjet reactor coupled to vacuum-UV photoionization was used to study the formation of higher hydrocarbons during the pyrolysis of allene. By use of this technique, a progression of intermediate species profiles including hydrocarbon radicals were obtained as a function of temperature at millisecond reaction times. Mass 80 was the first product species observed as temperature was increased which is consistent with early flow reactor studies of allene pyrolysis leading to the formation of predominantly the 1,2 isomer of dimethylenecyclobutane.

Our current work involves an analysis of a proposed mechanistic pathway for conversion allene to 1,2 dimethylenecyclobutane and subsequently to benzene and other higher hydrocarbons. A possible pathway for early benzene production during allene pyrolysis involves allene dimerization to 1,2 dimethylenecy-

butane followed by a multistep mechanism converting 1,2-DMCB to 1,3-hexadiene which goes through a higher activation energy, slower conversion mechanism to benzene through the cyclohexadienyl radical. A kinetic analysis using rate data for 1,3-cyclohexadiene to benzene conversion obtained by earlier investigators (7) shows that this route could account for the initial rate of mass 78 production observed experimentally. The higher hydrocarbon product distribution observed in particular the early formation of mass 120 supports the proposed allene dimerization to 1,2-DMCB. Future work will include resolution of mass 80 isomers to aid in the reaction pathway analysis. Data from earlier flow reactor studies can not be used to resolve these issues because of the intrusion of surface effects.

#### References

- 1a. Westmoreland, P. R., Dean, A. M., Howard, J. B., and Longwell, J. P., *J. Phys. Chem.* **1989**, *93*, 8171-8180; b) F. Communal, S.D. Thomas, and P.R. Westmoreland, "Kinetics of C<sub>3</sub> Routes to Aromatics Formation," Poster P40, 23rd International Symposium on Combustion, Orleans, July 22-27, 1990.
2. Boyle, J., and Pfefferle, L. D., "Methylacetylene and Allene Pyrolysis", presented AIChE Annual Meeting, Chicago Illinois, 12/90.
3. Blomquist, A. T., and Verdol, J. A., *J. Amer. Chem. Soc.*, **1956**, *78*, 109-112.
4. Meinert, R.N., and Hurd, C. D., *J. Amer. Chem. Soc.*, **1930**, *52*, 4540-4549.
5. Boyle, J., and Pfefferle, L. D., Lobue, J., and Colson, S., *Combust. Sci. and Tech.*, **1990**, *70*:187-203.
6. Boyle, J., PhD thesis, Studies of Pyrolysis and Oxidative Pyrolysis of Allene, Methyl Acetylene, Ethyl Acetylene and Butadiene using VUV Photoionization Mass spectrometry" Yale University, 1991.
- 7a. Benson, S. W., and Shaw R., *J. Amer. Chem. Soc.*, **1930**, *89*:21,5351-4549.
8. Weinstein, B., and Fenselau, A. H., *J. Chem. Soc. Section C*:368-372 (1967).
9. Ritter, E., Bozzelli, J., THERM: Thermo Property Estimation for Radicals and Molecules, Dept. of Chemistry, New Jersey Institute of Technology.
10. Kovacevic, K., Eckert-Maksic, M., and Maksic, Z. B., *Croatica Chemica Acta*, **1974**, *46*(4), 249-259.

#### Acknowledgements

The authors would like to acknowledge discussions about this work with Dr. Kiefer, and partial support from an NSF equipment grant.

Table 1

RELATIVE CONCENTRATIONS OF PRODUCT SPECIES  
DURING THE PYROLYSIS OF ALLENE 2ms, 600 Torr.

MOLECULAR WEIGHT	TEMPERATURE (K)					
	1280	1320	1450	1515	1545	1580
52	**	**	4.7	4.7	7	12
54	**	**	5.9	29	23	40
56	**	**	8.2	40	56	39
66	**	**	**	3.9	4.3	6
67	**	**	4.0	3.9	3.5	3.5
68	**	**	**	4.3	4.3	5
78		*	3.1	23	31	47.5
79		1.5	17	30	35	43.5
80	2.4	5	25	43	50.5	52
91			2.3	2	3.5	5.5
92			3.1	22	35	30
93			---	*	6	9.8
94			3.9	14	15	19.6
104			---	2.7	6.3	8.6
105				5.5	5.5	8.5
106			2.4	12.5	12	22
116				5.9	9.5	11.3
117			---	4.7	7.5	14
118				9.8	14	23
120			7.8	20.5	18	19
128					6.2	10
130					10.5	14
142				9	14.5	17
144			2.7	7	13	14.5
154					2	4
156				7	15	21
158			3.5	6.3	10.5	12
160				10	5	5
166					5	6
168						8.5
170					5	10
178					1	3
180					4.3	10

\* Species present in 0-1 unit

\*\* Species present in 1-2 units

Note: Only those hydrocarbon radical species with comparable concentration to the stable analog were included in this table.

Figure 1: Schematic of the VUV Photoionization Mass Spectrometer and Microjet Reactor Experiment

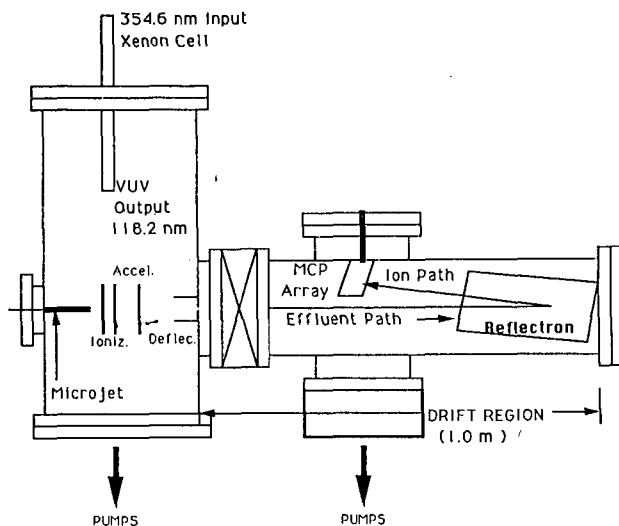


Figure 2: Equilibrium Constants for the Dimerization of Allene to the 1,2- and 1,3- Isomers of Dimethylenecyclobutane

